The above work was carried out in the Engineering Laboratories of Cambridge University, and I wish to express my sincere thanks to Prof. B. Hopkinson for his many suggestions and inspiring interest.

A Chemically Active Modification of Nitrogen, produced by the Electric Discharge.—VI.*

By the Hon. R. J. STRUTT, Sc.D., F.R.S., Professor of Physics, Imperial College, South Kensington.

§ 1. *Effect of Catalysts in Promoting the Formation of Active Nitrogen.*

There has been considerable controversy on the question of whether or not pure nitrogen would give the afterglow, which, as I have shown in the previous papers of this series, is associated with the presence of chemically active nitrogen.

E. P. Lewis[†] was disposed to think that the presence of oxygen or nitric oxide was essential, but in a much later paper,[‡] though still inclined to the same opinion, he states that the afterglow continually increased in intensity as the proportion of oxygen was reduced.

Warburg, in some experiments on the "luminous electric wind" in nitrogen at atmospheric pressure,[§] found that the intensity of the effect was much diminished by prolonged heating with sodium at 300° C., though he expressly states that he was unable to get rid of it altogether. It is not clear that the "luminous electric wind" (which was not bright enough for adequate spectroscopic examination) is the same phenomenon as the active nitrogen glow obtained at low pressures. Experiments made later in Warburg's laboratory by von Mosengeil[||] on the active nitrogen glow at low pressure led to the conclusion that it was not diminished by heating the gas with sodium in a closed discharge vessel.

In my own earlier experiments in which the presence of chemically active nitrogen was first demonstrated,* I employed various methods of preparing nitrogen, but obtained no indication that anything else than nitrogen was essential.

F. Comte† found that after very prolonged passage of nitrogen over hot copper a gas could be obtained which did not give the glow, and he was able to restore the glow by admission of minute quantities of oxygen.

Attempts were made by Koenig and Elöd‡ and by myself§ to repeat Comte's result, but without success. I had, indeed, frequently used hot copper purification before that time, and obtained the glow as usual.

In the note cited I described a technique of purifying nitrogen for this work by prolonged contact with cold phosphorus. It was made practically certain that such nitrogen could not contain one part of oxygen in 100,000, for admission of oxygen to that extent distinctly restored the luminosity and cloud formation which attend oxidation of moist phosphorus.

Shortly after Comte's publication E. Tiede‖ published some experiments which he regarded as confirming Comte's conclusion. Passing over these, which were not very strongly emphasised, we come to a publication of Tiede and Domcke¶ describing the preparation of nitrogen from barium or potassium azide. They found that nitrogen thus prepared gave no glow, but that the glow could be restored by admission of a trace of oxygen.

This experiment was repeated by Koenig and Elöd** and by myself, in collaboration with Prof. H. B. Baker.†† In each case the opposite conclusion to that of Tiede and Domcke was recorded. Prof. Baker and I also introduced the liquid alloy of sodium and potassium into a sealed vacuum discharge vessel containing rarefied nitrogen. The glow remained very bright even on prolonged standing. Tiede and Domcke in a third paper‡‡ returned to the use of hot copper. Bomb nitrogen was passed over copper heated to about 400° C., and the glow was almost completely got rid of. At high temperatures it returned, a result attributed to dissociation of any copper oxide that might be formed. No drying agents or other absorbents were used.

　* I, of this series.
　† 'Phys. Zeits.,' vol. 14, p. 74 (1913).
　‡ 'Phys. Zeits.,' vol. 14, p. 165 (1913).
　§ 'Phys. Zeits.,' vol. 14, p. 215 (1913).
　‖ 'Berichte,' vol. 46, p. 340 (1913).
　¶ 'Berichte,' vol. 46, p. 4065 (1913).
　** 'Berichte,' vol. 47, p. 523 (1914).
　†† 'Berichte,' vol. 47, p. 801 (1914).
　‡‡ 'Berichte,' vol. 47, p. 420 (1914).

Prof. Baker and I were unable to repeat this result.* The glow occurred admirably with the copper at any temperature up to a red heat.

Finally, J. de Kolowski, working with the electrodeless discharge, obtained the glow as usual with nitrogen which had been purified from oxygen by means of potassium.†

Tiede and Domcke argued from their experiments that there was no such thing as active nitrogen. The palpable weakness of this reasoning,‡ combined with the failure of Prof. Baker and myself to confirm either of the experiments which were described as so easy and certain of repetition, obscured from us the real value of their work. This was not realised until Tiede and Domcke came to London with their apparatus and materials and repeated their azide experiment at the Imperial College. The glow was much reduced, though (at all events in all the experiments made on this occasion) it was still conspicuously visible; when a trace of oxygen was admitted by heating a little silver oxide enclosed in the apparatus, the glow was restored. These results were obtained with a discharge tube like that illustrated in my first paper.§ Using a discharge tube like that shown in fig. 1, which has a large bulb in which the glowing gas accumulates, we did
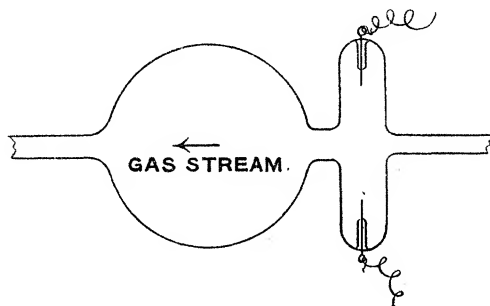

GAS STREAM.

Fig. 1.

not succeed in diminishing the glow much, if at all. These experiments were described jointly by Baker, Tiede, myself and Domcke.‖

During this visit a further attempt was made by Prof. Baker and myself,

* 'Berichte,' vol. 47, p. 1049 (1914).

† 'Comptes Rendus,' vol. 158, p. 625, March 2, 1914.

‡ The glow associated with the presence of active nitrogen is not obtained from ordinary nitrogen unless a trace of oxygen is present : therefore there is no such thing as active nitrogen—such was their argument. To obtain a clear view of the value of this kind of reasoning, apply it to the following more familiar case. Formation of sodium chloride by the interaction of sodium and chlorine is not observed unless a trace of moisture is present : therefore there is no such thing as sodium chloride.

§ I, p. 228.

‖ 'Nature,' vol. 93, p. 478 (1914).

with the benefit of such suggestions as Tiede and Domcke could make, to repeat their experiment with copper moderately heated, but with the same ill success as before. Dr. Tiede, if I understood him rightly, regarded the failure as due to some difference of our copper or crude nitrogen from that used by him in Berlin; but exactly what difference he was unable to say. During a brief visit it was impossible to go into the matter further.

After these joint experiments I felt that the position of the .question was very unsatisfactory. For, though now convinced that it was possible to prepare nitrogen which would give a much increased glow when oxygen was added to it, my previous conviction was unshaken that the phosphorus-purified nitrogen above mentioned, which gives the nitrogen glow excellently, did not contain oxygen to the extent of 1 part in 100,000.

It might, indeed, be possible to get out of the difficulty by assuming, with Tiede and Domcke, that almost incredibly minute quantities of oxygen were sufficient; but I soon found experimentally that this was not the case. In taking up the matter again after Dr. Tiede's visit, I sought to avoid the use of azide, the preparation of which in any quantity is troublesome and unpleasant, and not altogether free from risk. It was found that a sample of nitrogen which did not give much glow could be prepared by prolonged treatment of the commercial bomb nitrogen with sodium or potassium at 300° C. A flask A, fig. 2, of about 4 litres capacity, contained 10 or 20 c.c. of
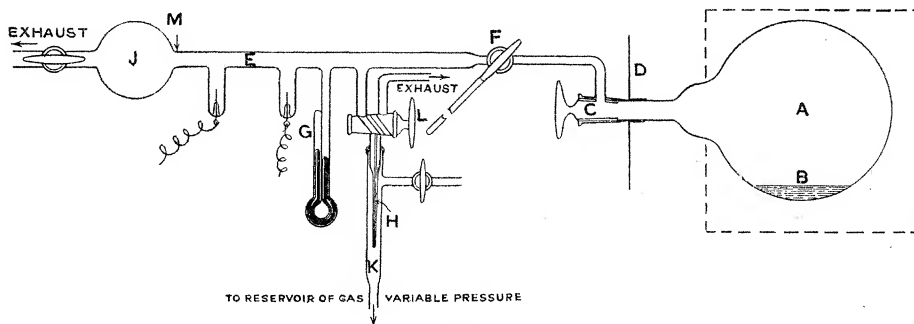

Fig. 2.

the liquid alloy of sodium and potassium.* The flask was in an asbestos oven (shown by dotted lines), with an electric resistance heater on the bottom. The flask was supported about an inch above the heater, and the temperature just under it was somewhat over 300° C. The lid of the oven was thin, so that the top of the flask was by no means so hot as the bottom, where lay the pool of alloy B. Thus a good circulation of the gas over the surface of

* This was introduced by means of a pipette, after the flask had been filled by displacement with bomb nitrogen.

the alloy by convection currents was assured. Some of the metal distilled on to the top of the flask, and also into the neck, which was necessarily kept cold, because of its greased stopcocks. A tin screen, D, in two semi-circular halves, carried on the neck, protected the latter from radiation.

Bomb nitrogen was admitted to this flask at a reduced pressure, so that on heating the pressure did not rise above the atmospheric. The heater was turned on after the gas had been admitted, and left on all night. In the morning the gas was allowed to cool, and was ready to be passed through the vacuum discharge tube E on its way to a Gaede pump. The regulating stop-cock F and the pressure gauge G enabled the pressure in E to be kept at a standard value of 6 mm., in spite of the gradual reduction of pressure in A during the experiment. Under these circumstances, the gas passing out through the pump measured 2600 litres per hour. A constant jar discharge was maintained between the platinum electrodes. The R.M.S. current measured on a Duddell thermo-ammeter was 7 milliampères.

Under these conditions the nitrogen afterglow was not bright, and it seemed to get dimmer still after a charge of the alloy had been heated several times with successive fillings of nitrogen. The glow still remained visible both in the neck and in the body of the bulb J. But it was reduced as low, or lower, than in the most successful experiment which Tiede and Domcke had shown us. Although the glow was feeble, there was no indication that what there was of it died out sooner than usual, as the stream of gas passed along the tubes leading to the pump. The proportion of oxygen necessary to get the optimum glow was investigated by means of the capillary inlet tube H,* by means of which air could be admitted. The capillary drew its supply from the outer tube K in which it was placed. K was connected with a large reservoir. The rate of intake could be adjusted by altering the air-pressure in this reservoir. Its exact value under given conditions was determined after the experiment by observing, with the manometer, the rate at which the pressure rose in the vacuum tube E, the volume of which was known.†

The stopcock used to shut off the capillary inlet at pleasure is necessarily made of much wider bore tubing than the capillary itself. Thus there is a considerable dead space between the capillary and the stopcock. Without

* The various capillaries used were drawn out in the blowpipe. After a little practice, capillaries can be drawn giving approximately the rate of intake desired. A special apparatus was used for testing them rapidly. Preliminary inspection with a magnifier is useful.

† With a capillary of non-uniform bore the intake of air into a vacuum bears no simple relation to the feeding pressure. Hence the necessity for determining it directly at each pressure.

special arrangements this would fill up with air when the stopcock was shut, and the accumulation would suddenly pass in when it was opened again, thus disturbing comparative observations. The difficulty was avoided by using a two-way stopcock as shown at L. When the flow through the capillary was not directed into the apparatus, the dead space was kept exhausted by a supplementary air pump, connected to the other branch of the two-way stopcock. When it was desired to observe the effect of admitting air, the stopcock was quickly turned through 180°, and the normal rate of inflow was at once established.*

A capillary was used which allowed 18 c.c. of air (measured at N.T.P.) to enter into a vacuum per hour from a reservoir at atmospheric pressure. This is equivalent to about 3·5 c.c. of oxygen per hour. By substituting pure oxygen for air, the rate of admission could be increased. By rarefying the air it could be diminished. In this way the following results were obtained :—

Oxygen admission.	Intensity of glow.
c.c. per hour.	
0 ·0	Faint.
0 ·4	No perceptible increase.
1 ·0	Distinct increase.
3 ·5	Strong glow.
18 ·0	No further increase.

It appears, then, that an admission of 3·5 c.c. of oxygen per hour produced about the maximum effect. Since the nitrogen flow was 2600 c.c. per hour, this represents an oxygen concentration of about 1/750 of the whole. If the oxygen admission is increased much beyond the quantities given in the Table, it begins to have a prejudicial effect. About 2 per cent. of it is enough to destroy the glow altogether.†

It appears, then, that in mixtures of nitrogen with oxygen the optimum effect is got when the oxygen present is something rather over one part in a thousand. Yet it had been clearly shown that nitrogen purified from oxygen by prolonged standing over phosphorus could not contain oxygen to the extent of one part in a hundred thousand, and yet nitrogen thus purified

---

* An alternative method, useful when direct intake from the atmosphere is desired, is to close the capillary with an indiarubber pad, brought up from below by a rack movement. In this case there is no dead space. When working with these very narrow capillaries it is necessary to be constantly alive to the possibility that they have become plugged by specks of dust.

† See V, p. 541.

gives the glow as well, or even better than nitrogen purified with hot sodium, to which the optimum percentage of oxygen has been added.

Minute admixtures other than oxygen are capable of performing the same function, and can act as catalysts for promoting the formation of active nitrogen by the discharge.

This was established by means of the apparatus already described, other gases being introduced into the tube from which the capillary drew its supplies. In these experiments I did not attempt to determine the optimum percentage of each admixture. A capillary was used admitting 3·3 c.c. of air per hour. The rate of admission of other gases by this tube would be somewhat different, depending upon the viscosities, which, however, do not vary widely. Roughly speaking, this capillary admits about 1/1000 part of foreign gas to the nitrogen stream under the standard conditions adopted.

It is to be observed that the purity, or dryness, of the added gas is not of the first consequence, since the total admission is so small. Impurity in it, in fact, only enters into the second order of small quantities. Still, reasonable care was taken.

Methane from aluminium carbide : strong restoration of glow. The quantity admitted was enough to slightly tinge the nitrogen afterglow with violet of the cyanogen spectrum, owing to reaction of methane with active nitrogen after the latter is formed. If the admission was stopped, the glow passed through a brilliant yellow stage of simple afterglow spectrum as the percentage of methane diminished, and then became very dim as the methane was eliminated. By experiments in which the feed of methane was at reduced pressure, it was found that 0·09 c.c. of methane per hour, 1/30,000 of the nitrogen flow, was enough to produce a perceptible effect.

Ethylene from sulphuric acid and alcohol, and *Acetylene* from calcium carbide, gave the same results as methane.

Carbon Monoxide from potassium ferrocyanide, washed with potash, strongly restored the glow, which was yellow, showing only a faint trace of cyanogen spectrum.

Carbon Dioxide induced a strong and pure nitrogen afterglow.

Sulphur Dioxide did the same.

Hydrogen Sulphide induced a specially bright and pure yellow nitrogen afterglow. When the entrance of hydrogen sulphide was stopped, it was not found that the glow passed off at all quickly or easily. Indeed, to reduce it to the point reached before admission of hydrogen sulphide, the tube had to be dismounted and washed out with aqua regia. It seems that exceptionally small traces of sulphur are sufficient to induce formation of active

nitrogen. These traces cling about the apparatus, probably in the solid state, with great obstinacy.

Chlorine, purified by fractional distillation of liquid chlorine, gave an absolutely definite though not very strong restoration of the glow. This case is peculiar, in that the glow restored by chlorine is notably greener than that obtained in other cases. The spectrum is the same as usual, but the yellow band is less intense relative to the green one. It is intended to study the question further, but it would seem as if chlorine atoms must remain in some kind of association with the atoms of active nitrogen, damping the vibrations which give rise to the yellow band. It takes time to get rid of this green tint. The chlorine seems to hang about the apparatus persistently.

Hydrogen was prepared from pure zinc and sulphuric acid, and freed from condensable impurities such as arsine, by passing through a tube packed with copper gauze and maintained at $-180°$ C. in liquid air. It was thought that a definite effect was produced in increasing the glow, but it was slight and difficult to observe, being much less in amount than in any of the previous cases.

Argon and *Helium*, each carefully purified, gave no observable effect.

The method of regulated admission by a capillary tube, so far used, is not easily applicable, except to permanent gases.

In addition, I have tried water vapour and mercury vapour, but the exact rate of admission was not measured in these cases.

A drop of *Mercury* was placed in a side tube, so that by warming it could be made to give off vapour which mingled with the nitrogen stream. Marked restoration of the glow was observed, though it was less brilliant than that observed with the best catalysts. The glow was tinged with green from the green mercury line, but, apart from this, there was marked brightening of the true nitrogen afterglow bands. The glass all round the mercury was carefully heated, so as to get rid of all adherent carbon dioxide or water vapour, and the effect of warming the mercury was repeatedly observed. There is no doubt of· the fact that the restoration is really due to mercury.

A drop of *Water* in a side tube was frozen in liquid air. As its temperature was allowed to rise very strong restoration of the glow was observed. The quantity of vapour soon became excessive and the glow diminished again, until it was destroyed altogether.

The relative efficiency of the various admixtures in inducing the nitrogen glow cannot be very satisfactorily compared, since no attempt was made to adjust each to its exact optimum amount, nor were any photometric measurements made. However, the following roughly approximate list

represents my general impressions.   The most effective substances are placed first :—

Hydrogen sulphide.	Oxygen.
Water.	Mercury.
Carbon dioxide.	Chlorine.
Carbon monoxide.	Hydrogen.

{ Acetylene.
  Ethylene.
  Methane.

{ Argon.
  Helium.
  Nitrogen.

It is then established that to obtain active nitrogen at all abundantly, it is necessary that a quantity of some foreign gas should be present to the extent of something like 1/1000 part.   This gas may be oxygen, or some compound of oxygen, but it may as well, or better, be sulphuretted hydrogen. Thus it is perfectly clear that, whatever the function of the admixture may be, oxidation of nitrogen has nothing to do with it.

In the controversy which has been reviewed it was maintained, on the one side, that pure nitrogen would give the full effect, and, on the other, that the presence of oxygen was essential.   It is now seen that, as in so many previous scientific controversies, neither side was entirely right.   Almost any contamination, with the exception of argon and helium, increases the yield of active nitrogen, as judged by the intensity of the nitrogen afterglow.

To exactly explain why each of the numerous experimenters quoted got the result he did would be too ambitious an attempt.   At the best there would be a large element of conjecture in it which could not be checked experimentally.   But a few suggestions may be offered.   Methods of purification, designed chiefly to remove oxygen, may result in the unintentional introduction of other substances which have the same effect in producing the glow that the oxygen itself had.   Carbonaceous impurities are, perhaps, the most likely to be concerned ; indeed I have frequently observed, particularly at high pressure, a trace of violet cyanogen in the nitrogen afterglow, when there was no other special reason to suspect the presence of carbon.   Unless my memory deceives me, this was observed in those experiments with azide nitrogen in a large globular discharge-vessel, made on the occasion of Tiede and Domcke's visit.   Visible cyanogen spectrum implies the presence of more than enough hydrocarbon to act as a catalyst and induce the glow.   The grease of stopcocks may, sometimes act as a source of carbon, particularly when stray electric discharges come in contact with it.

In experiments where oxygen is removed with hot copper, I suspect that carbon dioxide is very apt to remain in the gas.   Thus, in one attempt to

repeat Tiede and Domcke's experiment with copper at 400° C., the copper gauze employed had originally contained a great deal of paraffin oil used as a lubricant in the wire-drawing process. This was removed, as far as possible, by heating and oxidising the copper, which was afterwards reduced by plunging it in methyl alcohol and drying it in warm air. It would require special tests directed to that end to make absolutely sure that no carbonaceous matter remained after this treatment. If there was a trace, it would be oxidised by traces of oxygen in the nitrogen used, thus introducing carbon dioxide.

The gas which had stood over moist phosphorus also contained carbon dioxide, as was proved by bubbling it through baryta water. The amount of precipitate was decidedly more than the same volume of air gave under similar conditions, and thus indicates something like 1/1000 part of carbon dioxide, just such a quantity as would give the glow well. I have not particularly examined where this carbon dioxide came from—it is enough for the present purpose that it was there. In all probability phosphorus vapour would also induce formation of active nitrogen, though I have no definite evidence of the fact.

As regards earlier attempts to get rid of the glow by treatment with sodium or potassium : if the metals have been stored in oil (as potassium almost always is) enough hydrocarbons will probably cling to them to explain such experiments as that made by Prof. Baker and myself, allowing nitrogen to stand over the cold liquid alloy. But in any experiments on vacuum tubes charged with gas, and sealed up, the quantity of nitrogen present is so small that the absolute quantities of impurity needed are infinitesimal, and may be derived from the electrode or the glass. When a large quantity of nitrogen is purified and allowed to sweep through the apparatus, this source of contamination is practically eliminated.

These questions cannot be discussed in more detail, for lack of space. But, in short, it is easy to understand that methods designed to get rid of oxygen do not in general get rid of carbon compounds. The prolonged use of very hot sodium, however, is capable of removing both.

§ 2. *Probable Mode of Action of the Catalysts.*

If it is considered how diverse chemically the different catalysts are, it will not seem likely that their action can be interpreted by purely chemical considerations. We must remember that the impurity added performs its function, whatever that may be, inside the region where the electric current is passing. It is useless to add a trace of, *e.g.*, oxygen after the stream of

nitrogen has left the discharge, for in that case the addition produces no effect in increasing the yield of active nitrogen.*

The question is essentially one of processes occurring in the electric discharge, and must be considered in the light of our knowledge of the properties of electrons and gaseous ions.

In this connection the results of Franck† are very suggestive. He investigated the velocity with which negative ions travelled through nitrogen at atmospheric pressure, under potential gradients far too small to produce luminous discharge. It was found that with perfectly pure nitrogen the velocity was very large, indicating that the ions travelled over the greater part of their path as free electrons. A small admixture (something like 1 per cent.) of oxygen or chlorine diminished the mobility of the negative ions two hundred-fold, and made it about equal to that of the positive ions. In short, in pure nitrogen the negative ions were free electrons : the addition of a trace of oxygen or chlorine loaded them so that they became of atomic dimensions. Argon and helium, even when present in much more than traces, were unable to produce this effect.

Another property of pure nitrogen, namely, its capacity to yield active nitrogen under the discharge, is also extraordinarily influenced by a trace of oxygen or chlorine, but not by argon or helium. Can it reasonably be doubted that there is an intimate connection between the two sets of phenomena ? That the properties of a substance should be modified in this way by a large multiple when slightly contaminated is always surprising and exceptional. When we find two such cases running parallel, as these do, the suspicion of some connection becomes very strong.

* It is possible that someone casually glancing at this paper without being acquainted with its predecessors may be confused on this point. In the former papers I have studied the effect of adding various gases and vapours to active nitrogen after it is formed. In this case, of course, the addition is made by a tributary stream flowing into the stream of nitrogen *after* it has flowed past the place where electric discharge is maintained. In the apparatus, fig. 2, it would flow in at a side tube placed in some such position as M. But the present investigation studies the effect of added substances in assisting the production of active nitrogen. In this case the amount added is much smaller, and the addition is made *before* the nitrogen is submitted to electric discharge. Some substances have an important and distinct effect in both ways. Thus acetylene is capable of assisting formation of active nitrogen (pure yellow afterglow nitrogen bands) if a trace of it is added *before* the nitrogen is acted on by the discharge ; while, if introduced in larger quantities *after* the gas has been submitted to discharge, it unites chemically with the active nitrogen, forming hydrocyanic acid ; and, from the place where the acetylene flows in onwards, the yellow nitrogen glow is entirely replaced by a violet one showing cyanogen spectrum.

† 'Deutsch. Phys. Gesell. Verh.,' vol. 12, p. 613 (1910); see also vol. 12, p. 291 (1910).

Sir J. J. Thomson's experiments on positive rays* were made on the luminous discharge at low pressures, with the ions moving under large potential gradients, and thus under conditions approaching somewhat to those used for generating active nitrogen. Thus the information they yield with regard to the loading of electrons by atoms and molecules of various gases is more directly applicable than that obtained by the method used by Franck.

J. J. Thomson found† that negatively charged atoms of hydrogen, carbon, oxygen, sulphur, and chlorine were present among the rays which had passed through a hole in the cathode. Since such an atom had acquired its momentum in moving up to the cathode, it was necessary to assume that it had been positively charged while doing so, that it had picked up an electron subsequently which neutralised it, and then another which electrified it negatively. Some atoms appeared never to acquire a negative charge under these conditions. These were nitrogen, mercury, helium, argon, and the other rare gases.

It will be observed that, with the exception of mercury, the atoms which promote the formation of active nitrogen are precisely those which can become attached to an electron, while those which do not have this effect are precisely the ones which never become attached to an electron in the canal rays.

I think therefore it will be admitted that we have strong grounds for believing that the effect of certain admixtures in promoting formation of active nitrogen is produced by a loading up of the moving electrons in the discharge. In pure nitrogen the electrons are free. When a slight admixture of some gas containing, e.g., oxygen, sulphur or carbon, is present, atoms of the element introduced, set free in the discharge, attach themselves to the free electrons.

To develop the explanation further, some element of hypothesis is unavoidable. It will be supposed, as in previous papers, that active nitrogen consists of monatomic nitrogen. A nitrogen molecule is separated into atoms by the impact of a negative ion in the discharge. If, however, this ion consists of a free electron it is not so effective in administering the right kind of blow as when it is loaded so as to be of atomic dimensions. Hence the great increase in the production of active nitrogen when atoms of a kind suitable to effect this loading are introduced.

It may be asked, If an ion of atomic dimensions is needed, why do not the

---

* The title is unfortunate as applied to the particular experiments here quoted, which deal with negatively charged rays.

† 'Roy. Soc. Proc.,' A, vol. 89, p. 10 (1910); see also his 'Rays of Positive Electricity, p. 39, Longmans, 1913.

positive ions of nitrogen, which are present even when the nitrogen is absolutely pure, serve the purpose ? The fact that they move in the other direction cannot make the difference.

I think that this objection can be answered without additional hypothesis. The mean free path of an electron is greater than that of a positive ion, on account of its small size. If the positive ion is comparable in radius to the molecules of the gas, the ratio of free paths may be taken as 4 to 1. If, therefore, the electron only acquires its load towards the end of a free path it will have passed over a potential difference four times as great, and therefore have acquired four times the kinetic energy that a positive ion, which of course retains its atomic dimensions throughout, would possess. This possibility of possessing fourfold kinetic energy seems a sufficient explanation of why the negative ions should be so much more capable of producing active nitrogen than the positive ones.

It remains to discuss the exceptional case of mercury, which is moderately efficient in promoting formation of active nitrogen, but which does not take a negative charge in the canal rays. The mercury atom also shows an exceptional behaviour in the canal rays—it occurs with much larger positive electric charges than do other atoms,* the charge being in some cases as much as seven times the electronic charge. Such highly charged positive atoms in the electric field will acquire between collisions the large amount of kinetic energy which we have supposed necessary to administer the necessary shock to a nitrogen molecule. So that this exception may perhaps not unfairly be considered rather confirmatory than otherwise of the theory suggested.

As already mentioned, I have never been able to really reduce the glow to nothing, by any method of purification tried. It is difficult to decide whether this is possible, and even if it did seem to be accomplished in any experiment the doubt would remain whether somewhat different methods of stimulation† would not restore it. In the experiments described the glow was reduced to a point where the addition of 1/30,000 part of a hydrocarbon, such as methane, would distinctly improve it, so that to decide the question experimentally would be very difficult. It seems not inconsistent with the theory suggested that occasionally under favourable circumstances the impact of an unloaded electron might lead to formation of active nitrogen. If so, no purification could reduce the glow to nothing.

The above discussion has purposely been placed in a separate section of the

* J. J. Thomson, *loc. cit.*

† Particularly the electrodeless discharge at low pressures. It is certainly a matter of great difficulty even to appreciably reduce the glow in this case.

paper. If exception is taken to it as too speculative, it is hoped that the experiments of the preceding section will be judged independently.

§ 3. *Action of Active Nitrogen on Liquid Metals.*

It has been shown* that active nitrogen reacts with metallic vapours, yielding the nitrides. At the same time there is a development of the line spectrum of the metal. No apparent effect is produced when the active gas is passed over clean cold metals or over a film of mercury held on copper.† I now find that if a small quantity of mercury is placed in the bottom of a fairly wide U-tube, and shaken while the active gas passes over it, all luminosity is extinguished, and the mercury becomes foul, clinging to the walls of the vessel, as it does when treated with ozone. If the shaking is discontinued the glow again passes. After having treated the mercury in this way for a short time it is easily proved, chemically, to contain nitride. If water is added ammonia is formed, and can be distilled off and recognised by the Nessler reaction.

It is of interest to notice that when active nitrogen unites in this way with liquid mercury there is no development of the mercury spectrum. This is in contrast to what is found with mercury vapour, which gives the mercury spectrum strongly with active nitrogen. Other melted metals also react with active nitrogen. This was readily demonstrated with fusible metal (bismuth-tin-lead alloy) melting at about 100° C. Metals melting much above this temperature are less easily experimented with, because active nitrogen passes almost instantly into ordinary nitrogen by the catalytic action of hot surfaces.‡ Thus the active nitrogen is destroyed by contact with the heated walls of the glass tube containing the melted metal before getting to the latter. In spite of this difficulty it has been found possible to demonstrate the chemical action upon melted tin and melted lead. As in the case of liquid mercury, the spectrum of the metal is not developed.

§ 4. *Experiments with Other Liquids.*

These experiments with melted metals naturally suggested trying other liquids.

Since a stream of active nitrogen at low pressure can alone be used, we are limited to liquids of small vapour pressure. The glowing gas was bubbled§

* I, p. 224 ; V, p. 542.

† I, p. 225.

‡ See III, p. 363.

§ Bubbling is feasible with a "head" of 1 or 2 cm. of a light liquid. Active nitrogen cannot well be bubbled through molten heavy metals, because the pressure in the discharge tube which this would require would be unfavourable to formation of active nitrogen. Shaking the liquid in the stream of active gas must then be resorted to.

through glycerine in a U-tube without any apparent action. The glow got through quite well.

It was also bubbled through a concentrated solution of stannic chloride. Nothing was seen of the beautiful blue light developed when the vapour of this salt mixes with active nitrogen.

A dilute solution of indigo in concentrated sulphuric acid was slowly decolorised by bubbling active nitrogen through it. The exact nature of the action was not studied further, but the experiment clearly proves that active nitrogen is capable of acting on dissolved substances as well as on vapours and liquid metals.

§ 5. *Chemical Action on the Paraffins.*

Active nitrogen, it is agreed by all experimenters, acts freely on the majority of carbon compounds, with formation of hydrocyanic acid. Doubts, however, have been expressed as to its having this action on the paraffins.[*] I have re-examined this question as carefully as I could, with the advantage of having specially purified materials at command. In all cases abundant hydrocyanic acid was obtained.

Heptane.—The specimen was one which was specially purified by Sir Edward Thorpe.[†] Its origin was from *Pinus Sabiniana.* This was treated with active nitrogen for a few minutes, and an abundant precipitate of prussian blue, enough to colour several litres of water strongly, was obtained. The excess of oil, condensed out along with the hydrocyanic acid, had acquired a strong smell suggestive of nitriles.

Pentane.—The specimen was obtained through the kindness of Dr. A. G. Vernon Harcourt, F.R.S., and had been prepared for use in his standard lamp. It had passed the tests imposed by the Metropolitan gas referees for absence of olefines. This again behaved in just the same way as the heptane had done. The hydrocyanic acid was estimated quantitatively, and the yield was about the same as that formerly obtained[‡] with commercial light petroleum (motor spirit).

Methane.—The first sample was prepared from sodium acetate and soda lime and condensed with liquid air. It was then allowed to evaporate fractionally, the less volatile half of the gas being rejected. About 2 litres was retained for the experiment. After treatment with active nitrogen it yielded hydrocyanic acid equivalent to about 6 c.c. of nitrogen gas.

Two litres of methane prepared from aluminium carbide, and similarly

---

* Koenig and Elöd, 'Ber. d. Deutsch. Chem. Ges.,' vol. 47, Heft 4, p. 516 (1914).

† 'Chem. Soc. Proc.,' p. 299 (1879).

‡ V, p. 546.

purified by fractional distillation, gave about the same result as the fore-going.

With methane the cyanogen spectrum is not nearly so conspicuous as with some hydrocarbons; but if the conditions are suitably adjusted, with not too large a feed of methane, it is quite well seen.

§ 6. *Summary.*

1. The past controversy as to whether active nitrogen can be freely obtained from pure nitrogen, or whether a trace of oxygen must be present, is reviewed. It is shown that neither alternative is correct. Perfectly pure nitrogen will not give more than a little active nitrogen. On the other hand, to get a good yield it is not necessary that free oxygen or any oxygen compound should be present, for almost any small admixture of a foreign gas will enormously increase the yield of active nitrogen. The amount of admixture required to produce the best effect is usually of the order of 1/1000 part, but, to quote one case particularly examined, a very distinct effect is produced by adding a 1/30,000 part of methane.

2. The view is suggested that the impurity acts by loading the electrons in the discharge, and thus altering the character of their impact with the nitrogen molecules. This view is supported by the fact that gases carrying oxygen, sulphur, chlorine, carbon, and hydrogen are capable of promoting formation of active nitrogen. These are atoms which, according to the investigations of J. J. Thomson and Franck, are capable of attaching themselves to electrons in the discharge. On the other hand, argon, helium, and (of course) nitrogen itself, which are not able to load electrons, do not promote formation of active nitrogen. The case of mercury is at first sight anomalous, but reasons are given which seem to explain the anomaly.

3. Active nitrogen shaken with cold liquid mercury unites with it, forming nitride, but no development of mercury spectrum attends the action, as when mercury vapour unites with active nitrogen. Similar results have been obtained with other melted metals.

4. Active nitrogen bubbled through a weak solution of indigo in sulphuric acid slowly discharges the blue colour.

5. Active nitrogen acts freely on the purest heptane and pentane obtainable, with formation of hydrocyanic acid. On pure methane the action, though perhaps rather less, was still considerable. These experiments do not bear out the view that it is only olefine impurities in the paraffins that can yield hydrocyanic acid.